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Interaction of some 8-hydroxyquinoline-substituted and related ligands (see Figure 1) with various metal ions was evaluated by a calorimetric titration technique at 25 °C in MeOH. Bis-(8-hydroxyquinoline-2-ylmethyl)-substituted ligand **13** forms a very strong complex with Ba^{2+} (log K = 11.6 in MeOH) and is highly selective for Ba^{2+} over Na^{+}, K^{+}, Zn^{2+} and Cu^{2+} (selectivity factor > 10^6). The ^1H NMR spectral studies of the Ba^{2+} complexes with bis-(8-hydroxyquinoline-2-ylmethyl)- and bis(5,7-dichloro-8-hydroxyquinoline-2-ylmethyl)-substituted diaza-18-crown-6 ligands (**13** and **10**) suggest that these complexes are cryptate-like structures with two overlapping hydroxyquinoline rings forming a pseudo second macroring.

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Metal Ion Complexation Studies of Novel 8-Hydroxyquinoline-Containing Diaza-18-Crown-6 Ligands and Analogues

by

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Table 1. Log *K*, ΔH (kJ/mol), and $T\Delta S$ (kJ/mol) Values for Interactions of Macrocyclic Ligands with Metal Ions in Methanol Solution at 25.0 °C

ligand	cation	log *K*	ΔH	$T\Delta S$
1[a]	Na^+	2.89	-14.1	2.4
	K^+	3.39	-24.4	-5.0
	Mg^{2+}	6.82	-2.5	36.4
	Ba^{2+}	3.60	-11.6	8.9
	Zn^{2+}	5.12	-114	-85
	Cu^{2+}	10.1	-92.5	-34.9
	Co^{2+}	5.14	-91.1	-61.8
2[a]	Na^+	3.74	-26.4	-5.1
	K^+	6.61	-58.1	-20.4
	Mg^{2+}	b		
	Ca^{2+}	4.71	-25.2	1.7
	Sr^{2+}	4.67	-24.6	2.1
	Ba^{2+}	12.2	-76.1	-6.5
4	Mg^{2+}	5.7 ± 0.2	10.7 ± 0.9	43.2
	Co^{2+}	3.91 ± 0.08	-91.2 ± 0.5	-68.9
5	Mg^{2+}	5.02 ± 0.08	13.9 ± 0.9	42.6
	Co^{2+}	3.96 ± 0.06	-84.5 ± 0.5	-61.9
6	K^+	b		
	Ba^{2+}	3.57 ± 0.06	-29.4 ± 0.7	-9.0
	Zn^{2+}	4.80 ± 0.08	-64.8 ± 0.6	-37.4
	Cu^{2+}	5.01 ± 0.07	-57.6 ± 0.6	-29.0

...Continuation of Table 1

ligand	cation	log K	ΔH	$T\Delta S$
8	Na^+	~3[c]	~-5[c]	
	K^+	3.52 ± 0.03	-31.2 ± 0.4	-11.1
	Ba^{2+}	4.22 ± 0.05	-19.2 ± 0.8	4.9
	Zn^{2+}	> 5.5	-19.0 ± 0.5	> 12.4
	Cu^{2+}	4.28 ± 0.09	-55.3 ± 0.7	-30.9
13	Na^+	3.65 ± 0.01	-25.3 ± 0.2	-4.5
	K^+	5.88 ± 0.04[d]	-55.6 ± 0.7[d]	-22.0
	Ba^{2+}	11.6 ± 0.2[d]	-73.0 ± 0.5[d]	-6.8
	Zn^{2+}	4.92 ± 0.07[e]	-95.7 ± 0.6	-67.6
	Cu^{2+}	4.39 ± 0.09	-100 ± 1	-74.9
14	Na^+	3.02 ± 0.05	-20.0 ± 0.6	-2.8
	K^+	3.82 ± 0.02	-47.8 ± 0.3	-26.0
	Ba^{2+}	4.87 ± 0.04	-26.4 ± 0.4	1.4
	Zn^{2+}	4.80 ± 0.08	-64.8 ± 0.6	-37.4
	Cu^{2+}	(Brown Precipitate)		

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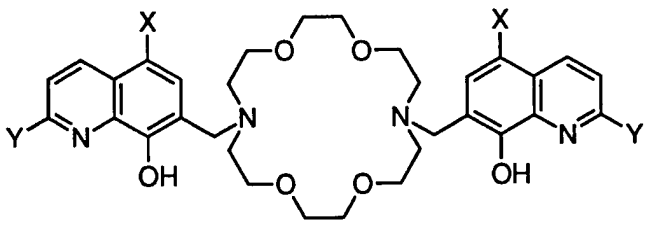
[a] Bordunov, A. V.; Bradshaw, J. S.; Zhang, X. X.; Dalley, N. K.; Kou, X.-L.; Izatt, R. M. *Inorg. Chem.* **1996**, *35*, 7229.

[b]No measurable heat other than heat of dilution indicating that ΔH or/and log K is small.

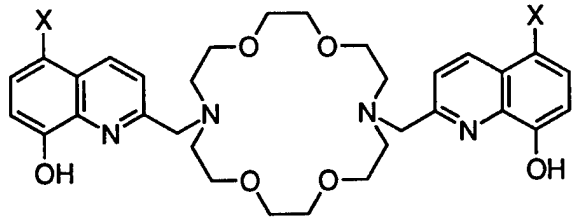
[c]Estimated by a competitive calorimetric titration with Zn^{2+}.

[d]Determined by a competitive calorimetric titration.

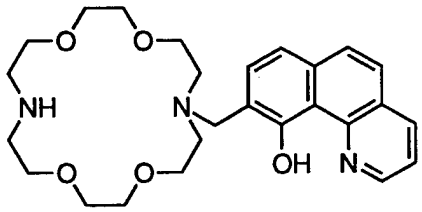
[e]When $[Zn^{2+}]/\mathbf{13} \geq 2$, a white precipitate formed.



1 X = Cl, Y = H
4 X = Y = H
5 X = CH_3, Y = H
6 X = H, Y = OH



2 X = Cl
13 X = H



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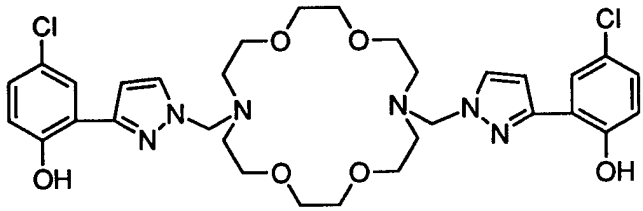

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Figure 1. 5-Chloro-8-hydroxyquinoline(CHQ)-substituted Diaza-18-crown-6 Ligand Analogues of **1** and **2** Used in this Study